Thermodynamic potential of a novel plasma-assisted sustainable process for co-production of ammonia and hydrogen with liquid metals

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Abstract

In the present article, the thermodynamic potential of a sustainable nitrogen fixation process for co-production of ammonia and hydrogen is investigated. The developed process takes advantage of chemical looping system by using a liquid metal such as gallium to the drive nitrogen fixation using three reactors including reactor R_1 to produce gallium nitride from gallium and nitrogen, reactor R_2 to produce ammonia and hydrogen from gallium nitride, and plasma reactor R_3 to convert gallium oxide to pure gallium. The results of the thermodynamic assessments showed that the proposed reactions are spontaneous and feasible to occur in the reactors. Likewise, the first two reactions are exothermic with $\Delta H = -230 \frac{kJ}{mol}$ and $\Delta H = -239 \frac{kJ}{mol}$ in the reactors R_1 and R_2, respectively with an equilibrium chemical conversion of 100%. The plasma reactor requires thermal energy to drive an endothermic reaction of gallium oxide dissociation with $\Delta H = +870 \frac{kJ}{mol}$. Thermochemical equilibrium analysis showed that the molar ratio of steam to GaN, pressure and temperature of the reactor R_2 are determining operating parameters identifying the final product of reactor such that by increasing the temperature, the ratio of hydrogen to ammonia (ψ) increases. However, by increasing the molar ratio of steam/GaN (φ), the ratio of hydrogen to ammonia promotes reaching 70% pure H_2 at 400 °C at φ=1.0. Then φ is decreased due to the unreacted steam appeared in the product. The equilibrium chemical conversion of all reactors is expected to reach the completion point (χ=100%) due to the highly negative Gibbs free energy of the liquid metal-based reactions and potentially due to the catalytic effect of the liquid metal together with the high heat and mass transfer coefficient offered by liquid metals at high temperatures. Finally, a scalability study points at a possible use of the new disruptive process design at small scale, and possible

industrial transformation scenarios for a distributed production at the local site of consumption are depicted in an outlook; based on previous evidence.

Keywords: Nitrogen fixation, ammonia production, hydrogen production, thermal plasma reactor, chemical looping, sustainability, zero carbon process.

1. Introduction

Energy production is one of the critical sectors in the development of a robust and dynamic economy of developed and/or developing countries, which can cause environmental pollution (water, soil and atmosphere) [1] and serious health issues [2] due to the continuous consumption of fossil fuels [3]. A census has been reached that despite efforts made to develop new technologies based on hybridisation with renewable energy resources, fossil fuels will remain the main energy supply for the next two decades [4]. Combustion is one of the well-established methods to release the energy content of fossil fuels, which is associated with the production of greenhouse gases (GHG) [5] and release of particulate materials (PM2.5) [6], CO_2 and other environmental pollutants. PM2.5 strongly contributes to the increase in the number of patients with lung and gastric cancers [7], while CO_2 is the main component severely affecting global warming and world climate change. Therefore, there is a need for further investigation aiming at developing new processes for the production of clean fuels such as hydrogen or alcohols, while decreasing the emission of GHG and pollutants to the environment.

Hydrogen is by far one of the promising clean fuels, which can be a replacement for fossil fuels. Hydrogen with lower heat value (LHV) of 120 MJ/kg, can produce water vapour during the combustion process, which in turn lowers the emission of carbon dioxide. In comparison with fossil fuels, hydrogen offers a higher LHV value, (e.g. 50-55 MJ/kg for natural gas vs. 120 MJ/kg for H_2) [8]. This can improve the thermal and energetic performance of the engines and/or processes operating with hydrogen, while reducing the costs associated with the design of the burners, reactors and combustors. The current pathway for the production of hydrogen is through reforming of natural gas, which is an energy-intensive process. Apart from the energy aspect, the reforming process delivers a large amount of CO_2 production to the environment as the process requires several reactors to increase the chemical conversion extent. To suppress the emission of greenhouse gases, catalytic reforming process was developed to lower the operating temperature, while suppressing the emission of GHG by increasing the chemical conversion of the reforming

reaction. Despite promising outcomes, the presence of the catalyst in the reactor is associated with challenge such as carbon deposition, catalyst sintering and deactivation [9], increasing the operating cost and complexity of the process [10]. The challenges are more intensified when catalysts require regeneration, which produces a large quantity of CO_2 and CO.

Another commercial pathway for the production of hydrogen is to utilise water electrolysis cells, which can also be hybridised with renewable energy to promote the economic viability of the process. Despite the hybridisation potential, the electrolysis cell has a low chemical efficiency (20 to 40%), high energy efficiency, which requires further improvement through passive technologies. Also, the challenges associated with the use of electrolysis such as robust energy storage for continuous production together with the corrosion of the electrodes require further investigation. Such challenges are the main barrier against the improvement in the technology readiness level of the electrolysis [11].

Apart from the production route, storage and safely transfer of hydrogen is another issue associated with the production of hydrogen at large scale and for industrial section. Hydrogen is a flammable and in some conditions an explosive gas, which requires specific levels of safety for the storage and use. Currently, most of storage pathways are expensive and require further development [12]. Recently special attention has been paid to the production of hydrogen carriers such as metal based compounds and ammonia [13, 14]. Such carries can directly be used as a fuel, intermediate or chemical product. Alternatively, they can safely be transferred to any end-user site considering the fact that knowledge and safety measures have already been developed for the transfer of ammonia from production sites to the consumption plants.

Chemical looping hydrogen production is a recently developed technology, which utilised two reactors namely the fuel and the air reactor. To supply the required oxygen for the hydrogasification or water-splitting reaction, solid metal oxide particles or a liquid molten metal oxide is used not only to provide a plausible heat and mass transfer, but to prevent any reactions between air and feedstock [15]. By doing this, nitrogen is avoided to appear at the outlet, which promotes the quality of the produced fuels. The concept of chemical looping has already been employed for syngas production, hydrogen production via sulphur/Iodin cycle [16], oxygen production [17, 18] and combustion purposes [19]. However, due to the limited operating temperature (e.g. $T < 1500$ °C), only specific metal oxides can be used in the system. This affects the efficiency of the process. Moreover, there are some challenges

such as sintering, particle breakage and particle deactivation, which add cost and complexity to the process [20, 21]. Therefore, more investigation is still required in order to improve the technology readiness level of the chemical looping technologies. Moreover, production of hydrogen and ammonia with chemical looping via water splitting requires high temperatures, which is technically challenging with the current technologies [22].

Ammonia (NH_3) is commercially produced through the nitrogen fixation driven by Haber-Bosch process (HB), which is an energy intensive process requiring high pressure to shift the equilibrium point inside the reactor [23]. Also, a catalyst with a high specific surface area is employed inside the reactor to increase the chemical conversion extent of the reaction. The HB process has extensively been studied in the literature and it has been shown that the process has reached its theoretical efficiency. Hence, investigation aiming at further decreasing the energy consumption of the process is not economically viable [24]. To bypass the challenges associated with the HB process, nitrogen fixation via sustainable chemical processes is one potential approach, which not only reduces the energy consumption associated with the process, but also increases the chemical conversion extent and economic viability of the ammonia production process. In a sustainable process, not only the side products, but also the energy produced in the process can be consumed by the process itself, while lowering the potential emission of GHG and environmental pollutants (e.g. CO_2, CO and H_2O). Also, depending on the quality and type of the end-user, the product of a sustainable process can be altered by a change in the operating parameters of reactors.

In order to develop a sustainable process, the reactions should thermodynamically be feasible to occur. For some reactions, due to the highly positive Gibbs free energy of the reaction (ΔG), conventional reactors are unable to drive the reaction. Hence, a specific type of reactor is required to maintain the required energy level for driving the reactions. Plasma reactor is one potential option, which can provide plausible heat and mass transfer medium, by consuming low energy in comparison with conventional reactors [25]. Plasma is the fourth state of the matter, which includes atoms, molecules, ions, cations, and electrons together with heavy particles [26]. Despite the charged species, the plasma environment is neutral. The plasma reactor can be categorised into different classifications of thermal plasma (hot, equilibrium) [27] and non-thermal plasma (cold, non-equilibrium [28]), which both have their advantages and disadvantages [29]. The main feature of a plasma reactor regardless of its type is to provide conditions to drive reactions with super positive Gibbs free energy [30]. If a hot plasma is used, almost all the reactive species have the same temperature and the

conversion of the reactor approaches the equilibrium conversion extent. However, for a cold plasma, of course, the chemical conversion is far from the equilibrium value, however from the economic and energetic performance point of view, the energy consumption for the cold plasma is lower than that of hot plasma [23, 31]. To justify the use of a cold plasma reactor for the sustainable process, it is required to promote the performance of the reactor with symbiotic, assisting techniques such as using super-porous nano-electrodes, which facilitate the conversion of the reaction at lower temperatures.

One example of using several such assisting techniques for plasma technology is a project referred to as "Surface-COnfined fast-modulated Plasma (SCOPE[1]), funded in 2019 by the European Research Council (ERC). Its holistic symbiotic concept encompasses reaction, catalytic, process and electrical engineering. This is believed to allow intensification of three chemical processes, including the ammonia production in a sustainable manner. The general idea in this project is to utilise cold plasma equipped with catalysis to improve the efficiency and chemical conversion of the reactor. The hope is, that the energy efficiency of cold plasma technology can be set into an economical business window and, on top of that, may open a new door for driving reactions that cannot be driven in a conventional reactor.

Nitrogen fixation is largely used for the production of fertilisers, which are key materials contributing to the agricultural sector, and this is taken as motivation for the present study. The estimated rate of global industrial nitrogen fixation is around 413 Tg/year [32], which includes the production of nitric acid and ammonia for industrial and agricultural applications. Up to 2010, the ammonia production rate was 120 TonN/year and about 80% of it was dedicated to the agricultural sector to produce fertiliser, which in turn exponentially contributed to the quality and quantity of food production. An environmental concern of the traditional pathway (the HB process) is the release of greenhouse gases (GHG) to the environment [33]. According to the energetic performance assessments, production of ammonia in an industrial scale is very energy intensive consuming ~36.6 GJ/ton of ammonia if natural gas is the main feedstock at practical efficiency of ~60% [34, 35]. For other feedstock (heavier hydrocarbon cuts as a feedstock), the consumption of energy reaches 169 GJ/ton of ammonia. Considering the environmental impact, a high quantity of CO_2 is directly or indirectly emitted to environment equivalent to 1.30 kg of CO_2/kg of ammonia, reaching 2.6 kg of CO_2/kg of ammonia [36].

[1] https://cordis.europa.eu/project/rcn/221198/factsheet/en

Considering the energy consumption and environmental concerns sourced from the industrial Haber-Bosch process as well as with the motivation to explore new production concepts such as distributed production at small scale, Anastasopoulou et al. [35, 37] conducted a comprehensive sustainability assessment plasma-enabled nitrogen fixation. They defined a three-stage filter including "integration of renewable energy", the "energy supply system for plasma reactor" and "process design for industrial plasma-assisted nitrogen fixation at small scale". It was identified that in order to develop a sustainable process at an industrial scale of 3650 tonnes/year, the most effective key parameter is to consider renewable energy such as solar or wind for maintaining the energy requirements of the plasma reactor. This will suppress the emission of GHG associated with the power production. Also, the synthesis and downstream unit profits from reconceptualization together with multi-object optimisation. The disruptive nature of the reactor expands to a leap potential for the entire plant design.

In another research, Anastasopoulou et al. [37] conducted a techno-economic assessment on a green route for small-scale production of fertiliser in Africa using renewable energy. They assessed the economic viability of the process by including solar photovoltaic and wind turbine and a hybrid configuration of both as a source of power for the plasma reactor. Over different scenarios, they found that utilisation of renewable energy requires large capital funding, however, it has the potential to reduce the final cost of energy, reduce the emission of GHG to environment and achieve sustainability. As Africa is the place for future large population and agricultural growth, this study has also a social dimensions, which is turned into as social incentive by the studies of the EU project AFRICA, funded through the Leap-Agri call[2].

In the present work, using the potential of plasma environment and plausible heat and mass transfer characteristics of liquid metals (here gallium), a new process is developed to take advantage of the nitrogen fixation reaction for the co-production of hydrogen and ammonia using a green process, which does not produce any GHG. Thanks to the features of the plasma, the sustainability circle of the process is completed. Hence, a thermochemical equilibrium model is developed to evaluate the effect of different operating parameters including the feed ratio, temperature and pressure of reactors on the production of ammonia and hydrogen. The thermodynamic stability phase diagram of the gallium in reaction with

[2] [2] https://cordis.europa.eu/project/rcn/221198/factsheet/en

other components is also studied and best operating condition is obtained using response surface methodology.

1. Conceptual process design

Figure 1 presents the schematic diagram of the process proposed for the co-production of hydrogen and ammonia using liquid metals and a plasma reactor.

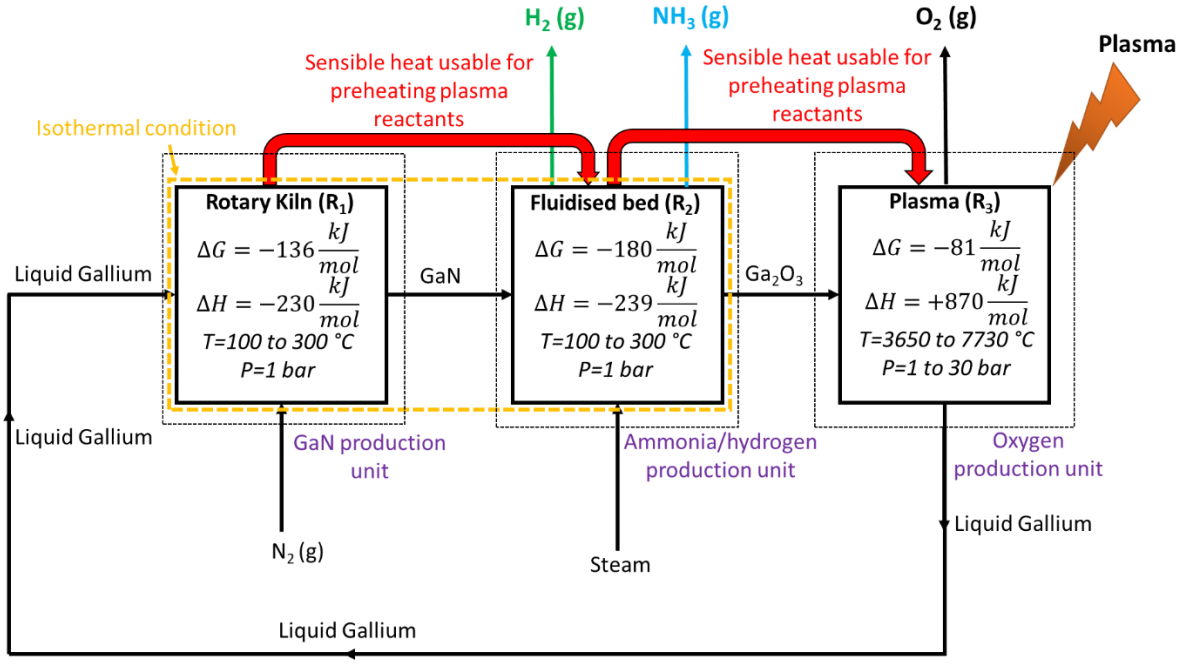


Fig 1a. Schematic diagram of the proposed process for a sustainable co-production of ammonia and oxygen using a novel plasma-assisted process.

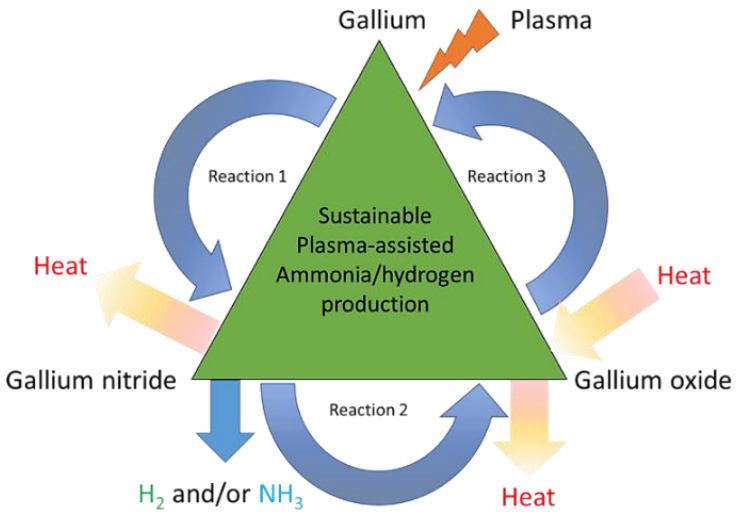


Fig 1b. A schematic diagram of the sustainable process proposed in the present research based on a novel plasma-assisted (project SCOPE).

In the present work, gallium (Ga) is proposed to be used as liquid metal and a medium for chemical reaction, which does not require high temperatures to form a stable liquid metal phase. Another advantage of gallium is that it is not corrosive at low temperatures. The melting temperature of gallium is 29.7 °C, which is not solidified at ambient temperature or might need a trace heating during winter when the room temperature is less than the melting point of gallium. The proposed system uses three reactors including reactor R_1 for gallium nitride (GaN) production from gallium (Ga) and nitrogen (N_2), reactor R_2 for ammonia, hydrogen and gallium oxide (Ga_2O_3) production from GaN and steam (H_2O), and reactor R_3 for dissociation of Ga_2O_3 and reproduction of gallium, which offers the sustainability of the process.

In reactor R_1, the following reaction occurs:

$$Ga(l) + \frac{1}{2}N_2 \rightarrow GaN \quad , \quad \Delta H_{373\,K} = -230\,\frac{kJ}{mol}. \tag{1}$$

The above equation is exothermic and the released thermal energy can partially be transported to another reactor using sensible heat carried by GaN solid particles. Due to the nature of the product, which is a slurry of liquid gallium and solid particles, a kiln rotary reactor is proposed which offers the following advantages [38]:

1) Sufficient residence time for contact between the gas, liquid and solid particles;
2) Great heat and mass transfer coefficient by providing effective rotating speed;
3) Capability to handle the continuous operation;

4) Compatibility to operate at low, mid- and high-temperature conditions;
5) High technology readiness level (commercially available).

The stability phase diagram of the gallium-nitrogen-oxygen system simulated with HSC chemistry software package is depicted in Figure 2. As can be seen, at temperature ranged between 100 °C and 300 °C, in an environment pressurised with nitrogen, the stable thermodynamic phases are GaN (s) and Ga (l). Hence, a slurry mixture of the components is expected to leave the reactor using slurry conveyor [39, 40]. With sufficient injection of nitrogen and an optimised ratio of N_2/Ga molar ratio, the quantity of GaN can be maximised, which is fed into reactor R_2.

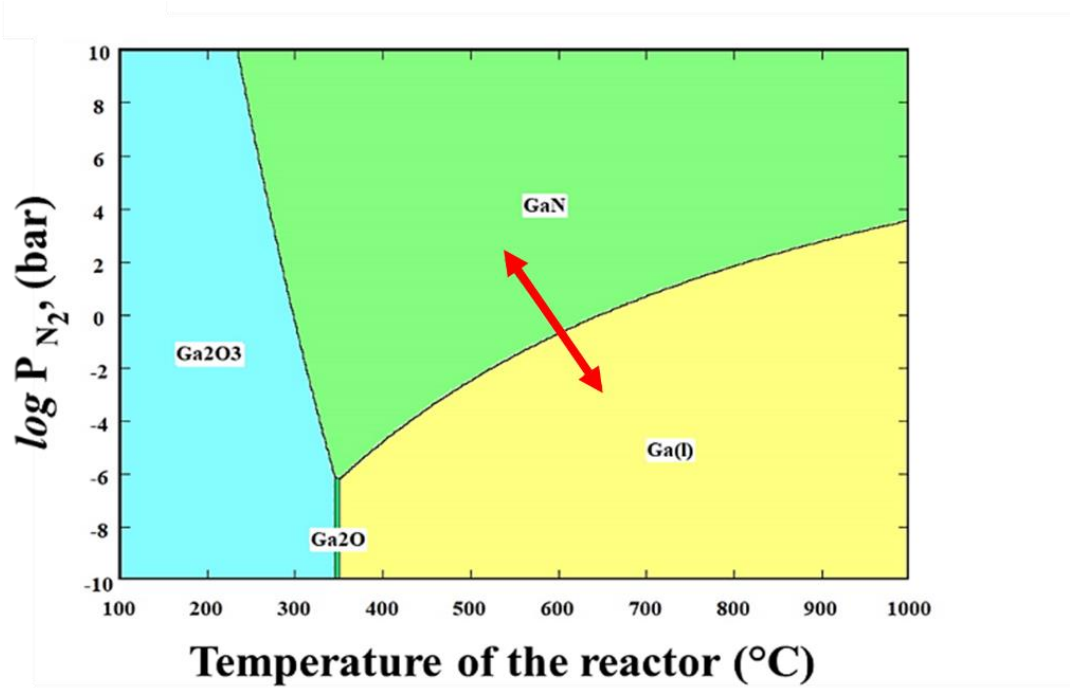


Fig. 2. The stability phase diagram of Ga-N-O thermodynamic system in reactor R_1.

In reactor R_2, the produced GaN reacts with steam to drive the nitrogen fixation reaction using the following reaction:

$$2GaN(s) + 3H_2O(g) \rightarrow 2NH_3(g) + Ga_2O_3 \quad , \ \Delta H_{373\,K} = -239\frac{kJ}{mol}. \tag{2}$$

Reaction 2 is highly exothermic and temperature can be self-maintained in the reactor once steam is injected in the system. The steam injection can provide a plausible mixing, while mainlining the temperature required for the reaction. Also, depending on the molar ratio of steam to GaN, the product can be ammonia, hydrogen or a mixture of both. It is worth saying that the morphology of the GaN particles can be non-uniform due to the operating conditions

of rotary kiln, thereby requiring a relatively robust heat and mass transfer system to drive the reaction to the completion point. That being said, solid particle fluidised bed is one potential reactor, which can offer the following advantages [41, 42]:

1) Uniform mixing between the particles and gases, which results in the uniform heat and mass transfer due to the sufficient collision of particles;
2) Symmetric and uniform temperature distribution along with the length and diameter of the reactor;
3) Capability to operate continuously;
4) Capability to separate carried-over particles by recovering and returning them to the reactor;
5) Ability to operate at various particle distribution size and morphology.

The outlet from reactor 2 is fed into the plasma reactor (reactor R_3), in which gallium oxide, which is a component with high positive Gibbs free energy is dissociated to liquid gallium and oxygen according to the following equation:

$$Ga_2O_3(s) \rightarrow 2Ga(l) + 1.5O_2 \quad , \Delta H_{373\,K} = +870\,\frac{kJ}{mol}. \tag{3}$$

Notably, the oxygen released from the process can be used in other applications (e.g. green houses or pure gas production units), which promotes the economic viability of the proposed process. The oxygen produced by the proposed process potentially requires less energy in comparison with air separation units and water splitting technologies, however, to prove this a robust techno-economic assessment must be conducted on the process once the energy requirement of the process is experimentally verified and evaluated. This is beyond the scope of the present investigation.

Figure 3 represents the stability diagram of the gallium-oxygen system for the plasma reactor to dissociate gallium oxide particles. As can be seen, the Gibbs free energy of the reaction is negative at T > ~4730° C, while the reaction is highly endothermic requiring ~1000 kJ/mol of energy to drive the reaction. Also, the stable phases are Ga_2O and Ga. Notably, Ga_2O can also be dissociated to Ga by reducing the partial pressure of oxygen and nitrogen in the system [43]. Normally, this can be done using a sweeping gas such as argon. Hence, the reactions in reactor R_3 is feasible at a minimum temperature of ~3230 °C, however, the equilibrium chemical conversion at this temperature barely reaches ~40%. At T > 4730 °C, the equilibrium chemical conversion extent reaches 100%. It is worth saying that such a high

temperature can locally be produced in a plasma requiring a robust and efficient quenching system to avoid any material corrosion, fatigue and thermal expansion. Currently, there are radiative systems in which by using high energy pulsed lasers, temperature can exceed 4730 °C for a short period of time, followed by a sudden quenching process [44]. Hence, developing a plasma reactor in this operating regime is technically challenging but possible with the current available technologies.

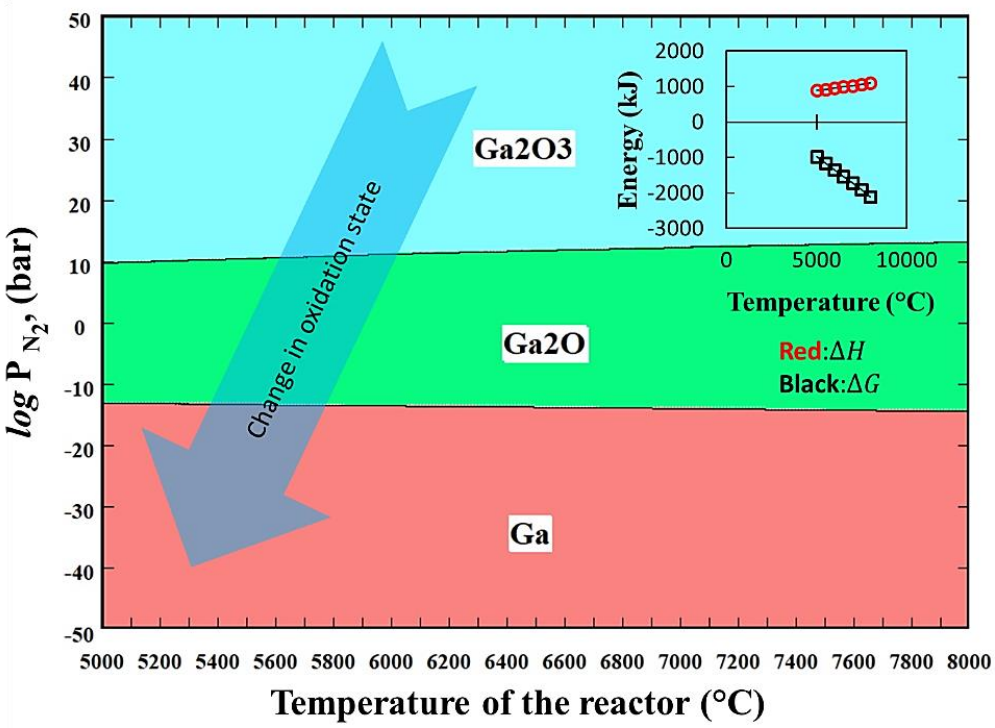


Fig. 3. The calculated stability phase diagram of Ga-N-O thermodynamic system in reactor R_3.

2. Methodology

To estimate the net enthalpy and the value of Gibbs free energy change for each reaction, the following equation was utilised:

$$\Delta M_{rxn} = \sum_{prod} \Delta M_i^f(T) - \sum_{react} \Delta M_i^f(T). \quad (4)$$

Here, M is a surrogate for either the enthalpy of the reaction, or the Gibbs free energy value belonging to component i. Also, the term $\Delta M_i^f(T)$ is either the net enthalpy of formation of component i or its Gibbs free energy of formation calculated at operating temperature of T.

The subscripts "*rxn*", "*react*" and "*prod*" stand for the term "reaction", "reactants" and "products", respectively. To conduct the simulations, Aspen Plus software package together with HSC chemistry 7.0 were employed using Gibbs minimisation method approach. For the plasma reactor, any reactive species including ions, cations and free electrons were taken into consideration. The valid phases were solid, liquid, gas, ion, cation and free electrons and/or positron. The thermochemical equilibrium module of HSC Chemistry together with R-Gibbs reactor were interlinked and used to assess the equilibrium performance of the plasma reactor. To calculate the thermo-physical properties of the components including heat capacity, standard enthalpy of formation, standard Gibbs free energy and density, Aspen properties and Hysys software packages were used, which were verified with the data reported by Barin et al. [45]. Uniquac and Peng-Robinson thermodynamic equation of states were employed and the estimated results were within ±0.5% of agreement against each other. To evaluate the scalability of the process, the system was simulated at $P > 5$ bar and 100 °C< $T < 300$ °C for reactor R2 to produce pure ammonia. The ratio of exergy transported by ammonia to the total energy input of the system referred to as exergy efficiency (χ) was selected as a criterion to assess the portion of energy input converted into chemical exergy shown in Eq. (5) as follows:

$$\chi = \frac{\dot{n}_{NH_3 \times LHV_{NH_3}}}{\sum Q_{net,R_z} + \sum_i^n n_i \times \Delta H_i} \quad (5)$$

Here, Q_{net} is the net thermal energy requirement for reactor z ($z=1,2,3$); n is an index for the species in the system including steam, nitrogen, ammonia, hydrogen, oxygen and gallium. Lower heating value (LHV) for ammonia and hydrogen was 18 MJ/kg and 120 MJ/kg, respectively. To assess the thermodynamic thermal efficiency of the system, following equation was used:

$$\chi = \frac{\dot{n}_{NH_3 \times LHV_{NH_3}}}{\sum Q_{net,R_z} + \sum_i^n n_i \times \Delta H_i} \quad (5)$$

Also, the thermodynamic thermal efficiency of the system was defined as a ratio of the outlet enthalpy values of the products to the total enthalpy introduced to the system by chemical compounds and steam considering 3% of inlet thermal energy as a heat loss to the environment.

$$\eta_{th} = \frac{\sum_{i=1}^{n} n_i \times \Delta H_i]_{out} - Q_{loss}}{\sum Q_{net,R_z} + \sum_{i=1}^{n} n_i \times \Delta H_i]_{in}} \quad (5)$$

Here, η_{th} is thermodynamic thermal efficiency of the system; Q_{loss} is the heat loss to environment calculated based on the equation given in the literature which is ~3% of total input.

3. Results and discussion

A series of thermodynamic equilibrium models were developed to assess the thermodynamic potential of the proposed process for the co-production of hydrogen and ammonia. In the following sub-sections, the effect of different operating parameters on thermodynamic performance and thermodynamic properties of the system is discussed.

3.1.Reaction's Gibbs free energy

Figure 4 presents the variation of the calculated Gibbs free energy and enthalpy of reaction on the operating temperature of the reactor R_1. As can be seen, the change in Gibbs free energy of the reaction is negative within the operating temperatures of 100 °C < *T* < 673 °C. Within the identified range of temperature, the reaction is spontaneous and the chemical equilibrium conversion reaches the completion point. For example, at T=300 °C, $\Delta G = -99.2 \frac{kJ}{mol}$ reaching $-61.6 \frac{kJ}{mol}$ at 500 °C. From 600 °C, $\Delta G > 0$, thereby requiring a non-conventional reactor to handle the reaction. Interestingly, within the above temperature range, the enthalpy of reaction is highly negative e.g. $\Delta H = -225 \frac{kJ}{mol}\ to - 231 \frac{kJ}{mol}$, showing that the reaction is exothermic. It is worth saying that the thermal energy released in the reactor is utilised to preheat the products and increase the temperature. Then the products are fed to reactor R_2. This will potentially reduce the thermal load of reactor R_2. The preheating of product occurs with the sensible heat absorbed from the reaction 1 considering the plausible thermal features of GaN particles such as heat capacity of 0.49 J/(gK) and thermal conductivity of 0.8-1 W/(mK).

Figure 5 represents the variation with temperature of the calculated enthalpy of reaction and the change in the Gibbs free energy of the reaction in reactor R_2. As can be seen, reaction is highly exothermic, while the reaction is spontaneously occurring within the operating temperature of 100 °C < *T*. For example, at *T*=373 °C, $\Delta G = -156\ kJ/mol$, while reaching -43 kJ/mol at *T*=1100 °C. Within the same temperature range, the enthalpy of reaction changes from -238 kJ/mol to -226 kJ/mol. Interestingly, the released thermal energy from both

reactors R_1 and R_2 can be used to preheat the products before introducing them to the plasma reactor. This in turn reduces the thermal load of the plasma reactor, which promotes the energetic performance of the process.

In Figure 6, the enthalpy and the change in the Gibbs free energy of the reaction in plasma reactor R_3 is depicted. As can be seen, the Gibbs free energy of the reactor is negative at $T >$ 3230 °C showing that reaction 3 is thermodynamically feasible to occur in a plasma reactor. Also, the reaction is super endothermic requiring a large amount of heat to be dedicated to the reaction, although part of the heat can be supplied from reactors R_1 and R_2. For example, at T=3230 °C, $\Delta G = -11 \frac{kJ}{mol}$, reaching $\Delta G > -541 \frac{kJ}{mol}$ at $T >$ 6230 °C.

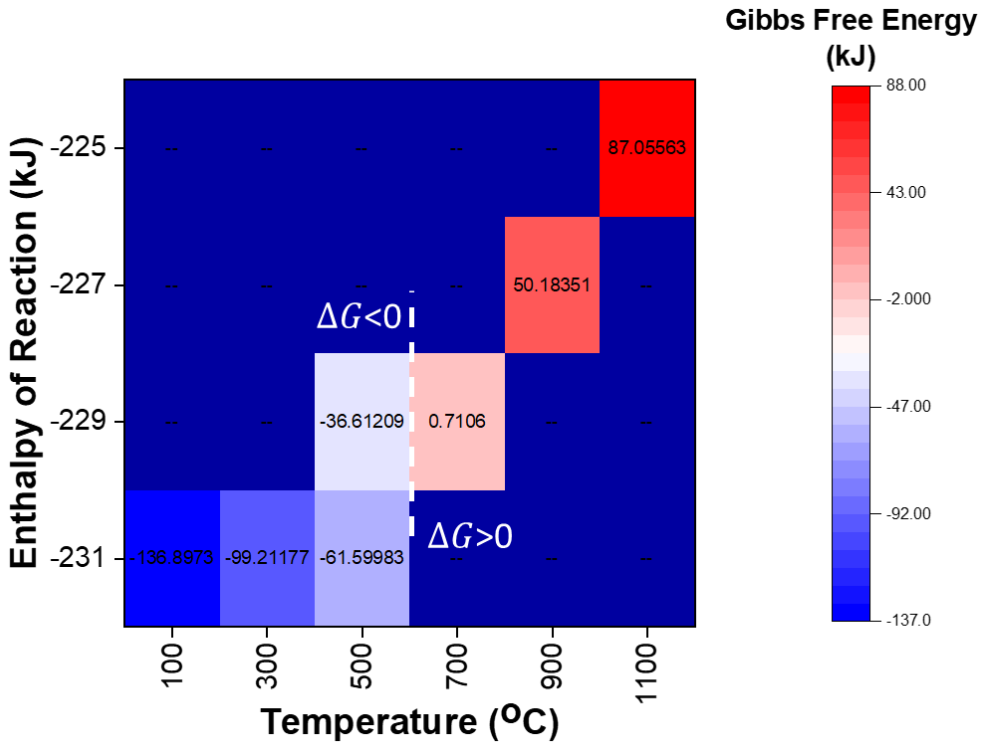


Fig. 4. The calculated dependence on temperature of the enthalpy of the reaction (ΔH) and the Gibbs free energy of the reaction (ΔG) in reactor R_1.

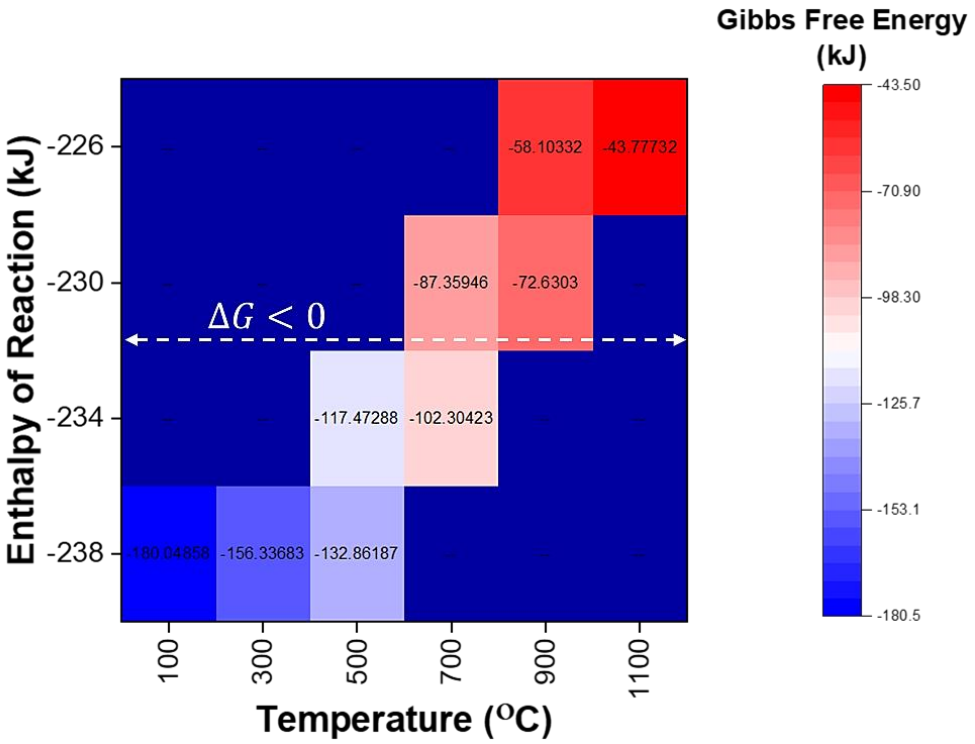


Fig. 5. The calculated dependence on temperature of the enthalpy of the reaction (ΔH) and the Gibbs free energy of the reaction (ΔG) in reactor R_2.

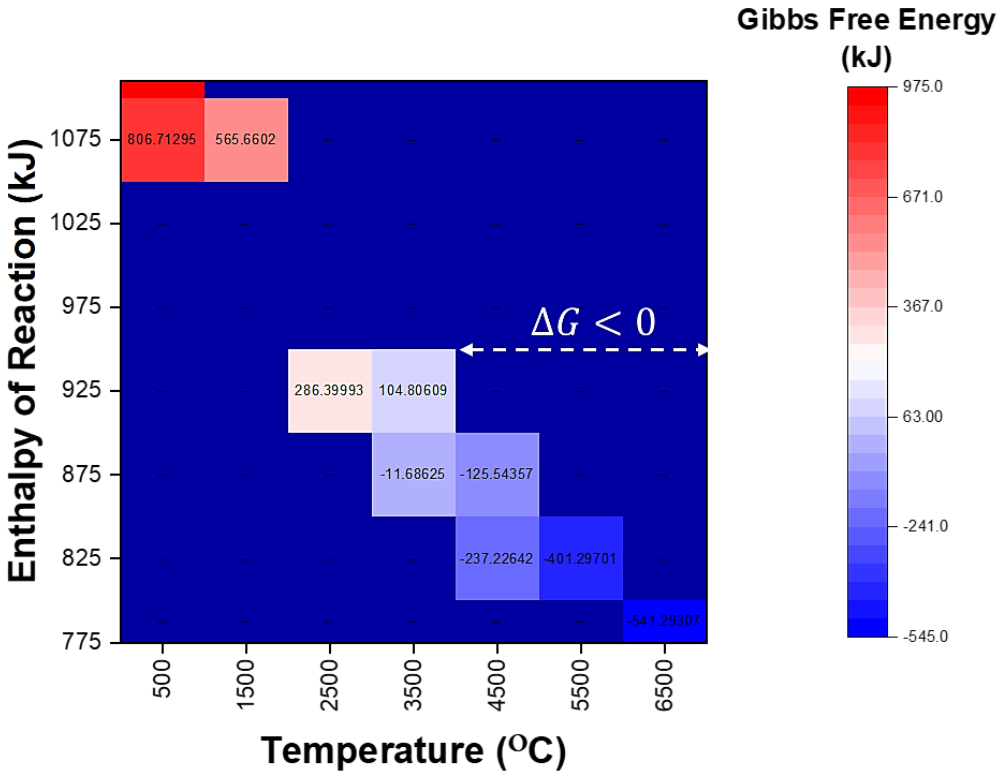
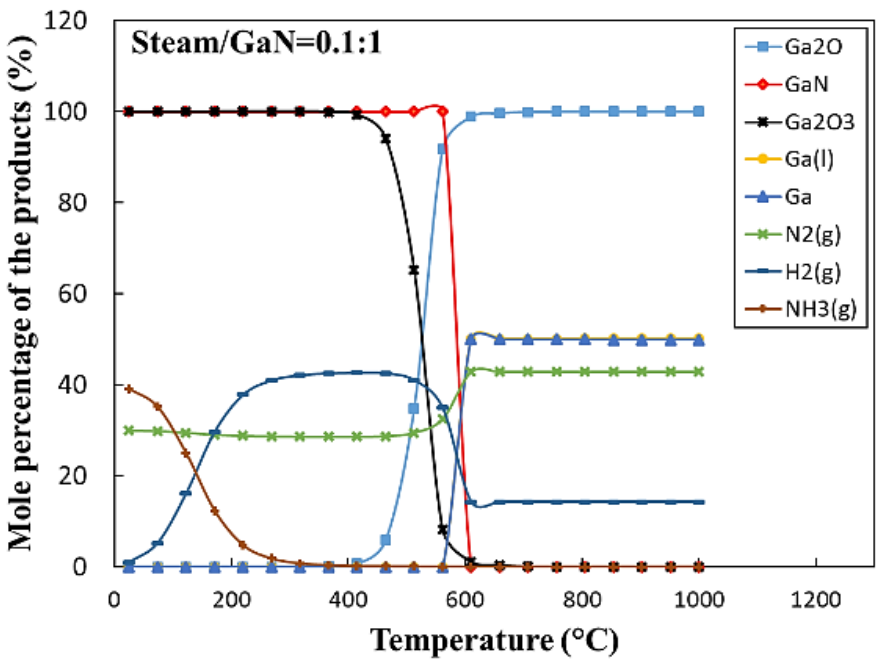


Fig. 6. The calculated dependence on temperature of the enthalpy of the reaction and the Gibbs free energy of the reaction in reactor R_3.

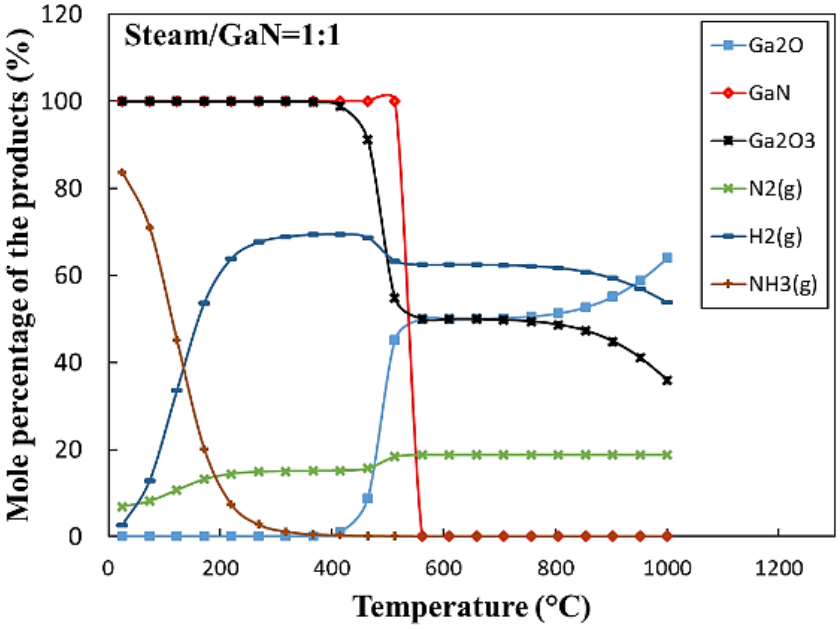
Reactor R_2 as perceived from Figure 1 is the heart of the process by which the main products are produced, while reactor R_3 is a complementary element to close the chemical loop and guaranty the sustainability of the proposed process by dissociating Ga_2O_3 to Ga, which cannot occur in a conventional reactor. Hence, these reactors are further investigated to identify the suitable operating parameters, in which the production of hydrogen and/or ammonia is maximised.

3.2.Reactor R_2

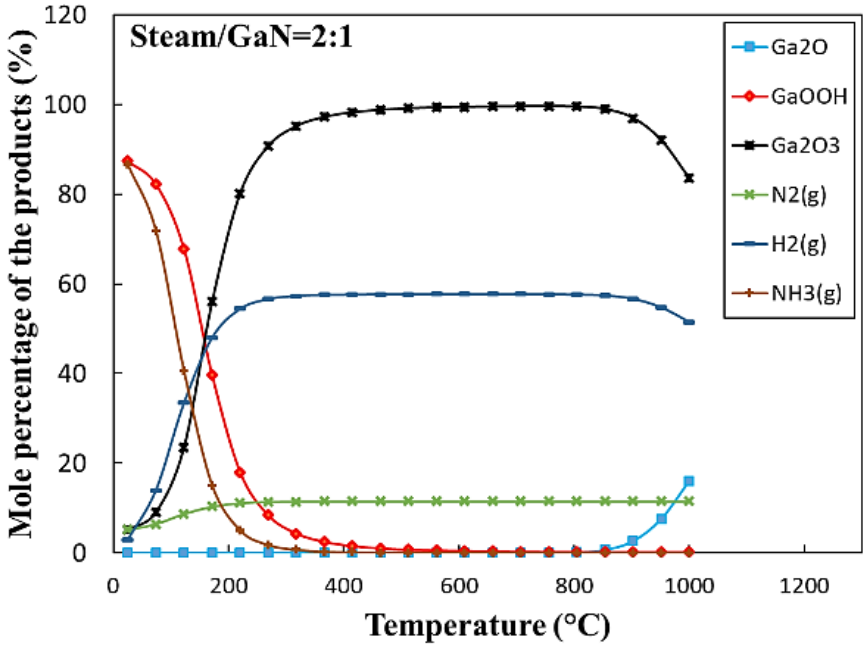
Figure 7 represents the variation of the mole fraction of the products of reactor R_2 with the temperature of the reactor for various steam to gallium nitride molar ratios (φ). As can be seen, regardless of φ, within the operating temperature range of 100 °C < T < 400 °C, the main product of the reactor is ammonia, Ga_2O_3 and H_2, therefore, this can plausibly be the optimised operating temperature for this reactor. For example, at φ=0.1, the mole fraction of hydrogen changes from zero to ~40%, while that of ammonia decreases from ~41.5% to zero. Hence, there is a thermodynamic equilibrium trade-off behaviour identified between the production of hydrogen and ammonia in reactor R_2 such that the final product of the reactor can be regulated depending on the end-user needs, storage facility and the application of the fuel by changing the operating conditions of the reactor. Interestingly, by increasing φ to 1.0, the production of ammonia and hydrogen is promoted to ~81% at 100 °C (for ammonia) and ~70% (for hydrogen) at 400 °C. With further increase in φ value, the unreacted steam appears in the outlet of the reactor, which in turn decreases the mole fraction of the target products, while adding an extra thermal load to the process. This is because water should be eliminated from the products before they can be fed into the plasma reactor. This requires a robust heat exchanger to recover the steam and inject it back to the reactor. This factor can considerably affect the economy of the process since steam production can be expensive. It is worth saying that if the excess steam is not extracted from the reactor, a side reaction between gallium and steam proceeds resulting in the production of Ga(OOH), which is an amorphous stable phase of gallium hydroxide. The presence of Ga(OOH) in the plasma reactor can produce H^+, which aggressively attacks other ions and molecules due to the “ionisation impact” in the reactor. Hence, there is an optimum point for the ratio, which can be identified through optimisation or experiments.


Steam/GaN=0.1:1
Mole percentage of the products (%)
Temperature (°C)
Ga2O
GaN
Ga2O3
Ga(l)
Ga
N2(g)
H2(g)
NH3(g)
0
20
40
60
80
100
120
0
200
400
600
800
1000
1200

(a)


Steam/GaN=1:1
Mole percentage of the products (%)
Temperature (°C)
Ga2O
GaN
Ga2O3
N2(g)
H2(g)
NH3(g)
0
20
40
60
80
100
120
0
200
400
600
800
1000
1200

(b)



(c)

Fig. 7. Results of the thermochemical equilibrium analysis of reactor R_2 at various molar ratios of steam /GaN (φ), a) φ= 0.1, b) φ=1.0, c) φ=2.0.

3.3.Reactor R_3

Figure 8 shows the calculated dependence of the mole fraction of the products of reactor R_3 on temperature. As can be seen, the chemical conversion extent reached the completion point (χ=100%) for Ga_2O_3 (the black line) by dissociating Ga_2O_3 to Ga, Ga_2O and O (g). However, by increasing the temperature of the plasma regime, Ga_2O is further dissociated to Ga and O_2. Hence, the final product of the reactor is gallium and oxygen which should rapidly be quenched and separated. The oxygen can be used for further applications, while gallium is returned to the reactor R_1 for nitrogen fixation reaction. Notably, at T > 4730 °C (5000 K~0.43 eV), reactor R_3 reaches an equilibrium state in which gallium and oxygen are the main products with a constant mole fraction. Hence, this temperature is an optimum temperature for the plasma reactor.

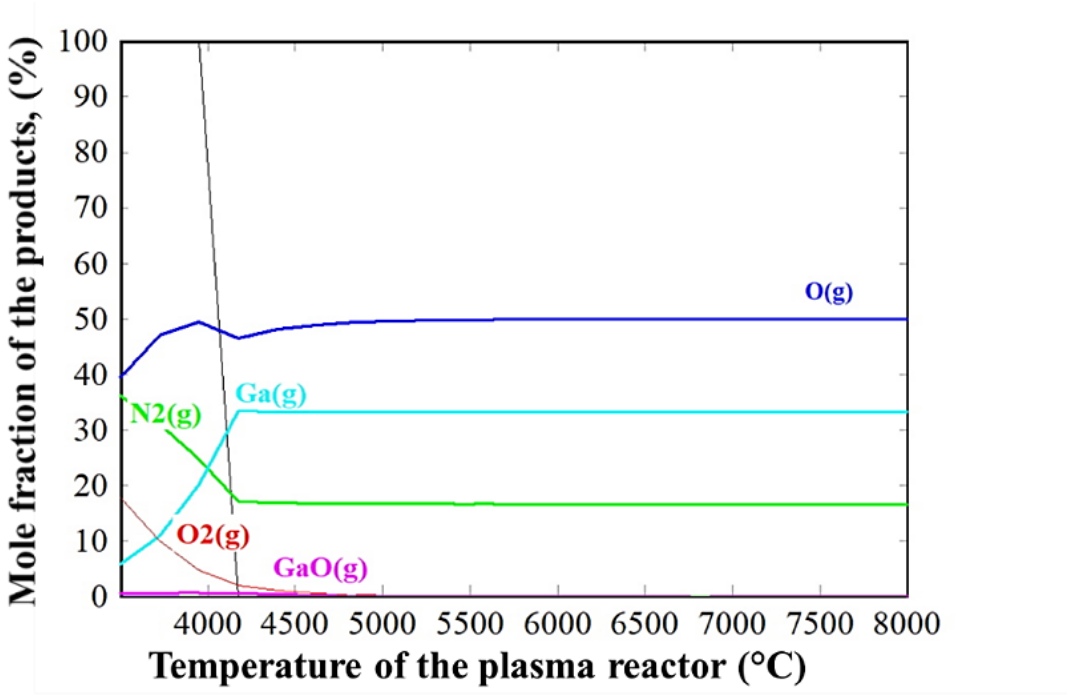


Fig. 8. Variation of the mole fraction of the products on the temperature for the plasma reactor R_3.

In Figure 9, the effect of the pressure of the reactor on the mole fraction of the products of the reactor R_3 is depicted. As shown, by pressuring the plasma reactor, gallium oxide (Ga_2O) forms massively in the reactor, which can add complexity to the operation of reactor R_1 once it is fed to the reactor. The formation of Ga_2O creates a non-reactive phase of gallium, which does not participate in the reaction. Hence, there would be a need for making up the gallium content through an external stream of liquid metal, which would be a barrier against economic viability of the process by considering the fact that gallium is a scarce and expensive material. Commensurate with this, it is recommended no to pressurise the plasma reactor. Notably, it also reduces the production of oxygen as well, which in turn suppresses the advantage of oxygen production in the process.

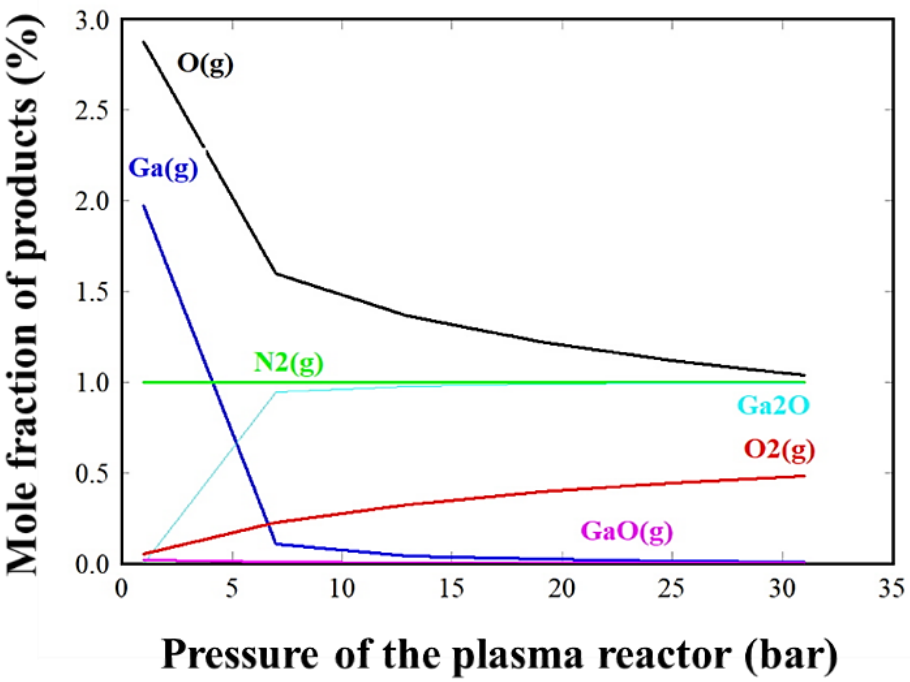


Fig. 9. Variation of the mole fraction of the products on the pressure of the plasma reactor R_3.

3.4.Optimisation with response surface methodology

Response surface methodology (RSM) is a chain of statistical, mathematical and theoretical methods for design and optimisation of the complicated experiments and processes, where there is limited data obtained by simulations and/or experiments [46]. An RSM model employs input parameters including operating conditions of the process and a target parameter to evaluate the sensitivity of the target parameter to those operating conditions and chooses the best ones, in which the target parameter is maximised or minimised [47]. It is worth saying that the decision-making algorithm of the model strongly depends on the response of the system to a change in the operating parameters. The responses can be collected by experiments or by conducting high-fidelity simulations.

In the present work, we report the results of an optimisation based on Box-Behnken approach using RSM technique to identify the sensitivity of the production of ammonia and/or hydrogen to each of the operating parameters. Of course, only reactor R_2 was assessed as it is the heart of the process, directly determines the mole fraction of the products. Figure 10 shows the algorithm of solution for the RSM model developed in the present work. As can be seen, the algorithm of solution has five main stages. After creating the matrix of the model (stage 1 and 2), a series of simulations are conducted based on the operating conditions given in Table 1 developed by RSM. For each iteration, the response is collected from the

simulation results and the optimisation is conducted once all twenty iterations are successfully conducted. It is worth saying that in the present work, the target parameter is the ratio of hydrogen to ammonia (ψ).

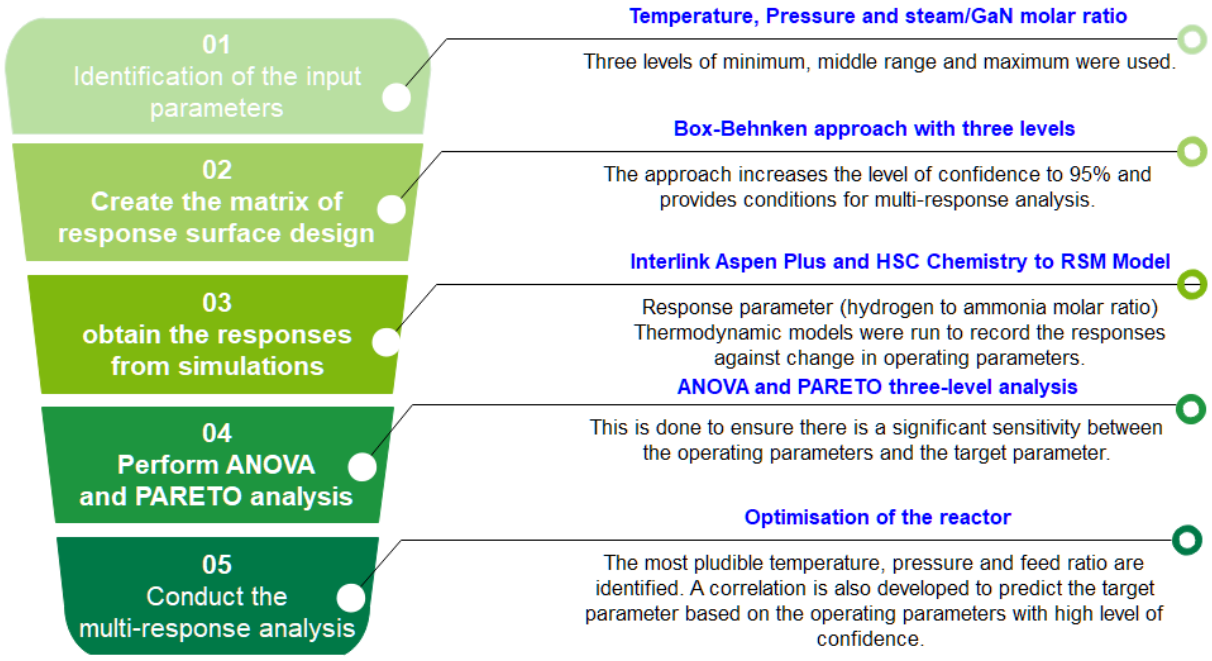


Fig. 10. Algorithm of the solution (flow diagram) for the RSM model developed in the present research.

According to the RSM model, initially, the input Table is created for temperature, pressure and steam/GaN molar ratio (φ) as identified in the thermo-chemical equilibrium analysis in the previous sections. As represented in Table 1, each operating parameter has three levels including minimum value (-1.0), middle value (0) and maximum value (+1.0). These values for temperature are 100 °C, 250 °C and 400 °C, and for pressure are 1 bar, 15 bar, 31 bar, and for φ are 0.1, 1.05 and 2, respectively.

Table 1. The response surface design matrix created with RSM model (randomized).

Run	Temp.	Press.	Steam/GaN
1	0	0	0
2	-1	1	1
3	1	-1	1
4	0	0	0
5	0	1	0
6	0	0	1

7	0	0	0
8	1	1	1
9	0	0	0
10	1	1	-1
11	-1	1	-1
12	-1	0	0
13	0	0	-1
14	0	-1	0
15	-1	-1	-1
16	0	0	0
17	1	-1	-1
18	0	0	0
19	-1	-1	1
20	1	0	0

Over 20 runs of simulations, the responses were recorded and used in the model to evaluate the sensitivity of the target parameter (ψ) to the operating conditions. As can be seen in Figure 11, the Pareto analysis shows that the most important parameter is the temperature of the reactor R_2, which considerably affects its equilibrium chemical performance. As shown in section 4.2, to produce hydrogen and ammonia or combination of both, the temperature of the reactor must be narrowed down to a specific range. Also, a trade-off was identified between the production of ammonia and hydrogen. Hence, temperature was a key parameter in the equilibrium simulations, which was also identified by the Pareto analysis based on the RSM model as well. Interestingly, it was found that not only temperature (A), but also pressure (B) and an interaction between the temperature and pressure (AB) contribute to the performance of the reactor. Hence, through multi-response analysis, the sensitivity of the target parameter to the temperature and pressure of the reactor was assessed. Notably, the model identifies that the steam/GaN ratio (φ) has no effect on the performance of the reactor. This parameter only determines which chemical component can be the dominant product of the reactor, which has already been identified through equilibrium analysis. Figure 12 represents the normal plot of the standardised effects of different operating conditions on ψ value for reactor R_2. As can be seen, amongst all the potential interactions between the operating parameters (binary, ternary…), only temperature, pressure, and the interaction between temperature and pressure can affect the performance of the reactor, which is in-line with the results obtained from the Pareto analysis. Also, it is in accordance with the results obtained with ANOVA analysis, by which it was identified that the change in ψ value is significant when temperature and pressure values change in the reactor. Likewise, the values obtained for the standardised effects are far from the insignificance line (see Figure 12), which confirms the justifications discussed in the previous sections. The detailed results of the ANOVA test are given in Table 2.

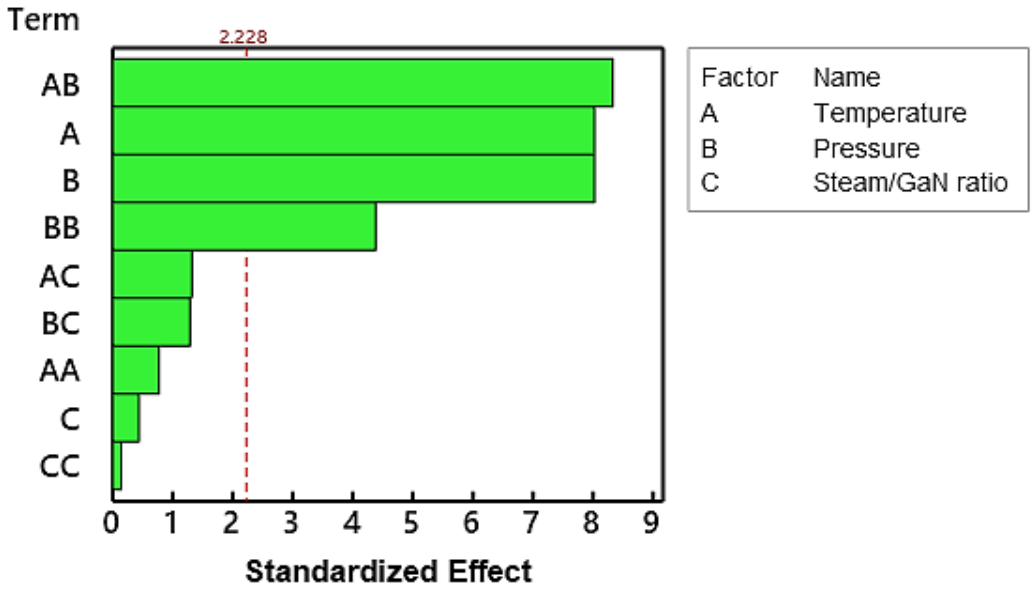


Fig. 11. The Pareto chart obtained with RSM for reactor R_2. Axial line α=2.228 is the significance line. Any parameters with value > α is an effective parameter.

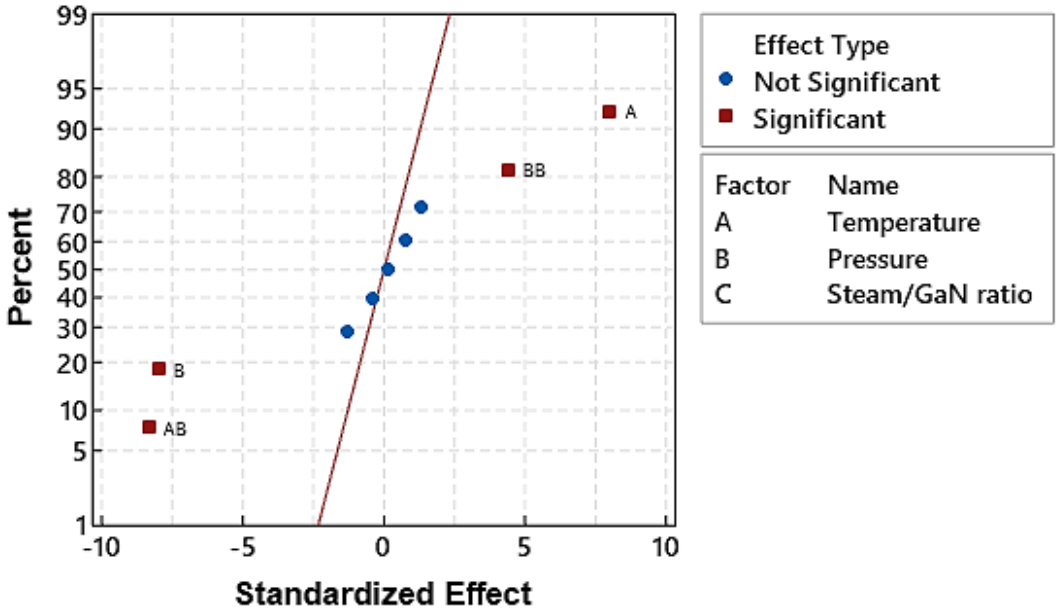


Fig. 12. The effectiveness of different operating parameters on the target (molar ratio of hydrogen to ammonia) for reactor R_2.

Table 2. Detailed results obtained from ANOVA analysis conducted on the sensitivity of the operating parameters on the target value.

Source	DF	SS	Contribution	Adj SS	Adj MS	F-Value
Model	9	30711	96.%	30711	3412	27.1
Linear	3	16009	50%	16232	5410	42.9
Temperature	1	8080	25%	8080	8080	64.1

Pressure	1	7864	24%	8077	8077	64.1
Steam/GaN ratio	1	64	0.2%	23	23.5	0.1
Square	3	5567	17%	5567	1855	14.7
Temperature*Temperature	1	2998	9%	75	74	0.6
Pressure*Pressure	1	2566	8%	2410	2410	19.1
Steam/GaN ratio*Steam/GaN ratio	1	2	0.01%	2	2	0.02
2-Way Interaction	3	9135	28%	9135	3044	24.1
Temperature*Pressure	1	8708	27%	8708	8708	69.1
Temperature*Steam/GaN ratio	1	218	0.6%	218	218	1.7
Pressure*Steam/GaN ratio	1	208	0.6%	208	207	1.6
Error	10	1258	3%	1258	125	

Source	**P-Value**
Model	0.001
Temperature (***T***)	0.001
Pressure (***P***)	0.001
Steam/GaN ratio (***φ***)	0.67
Temperature*Temperature	0.45
Pressure*Pressure (***PP***)	0.001
Steam/GaN ratio*Steam/GaN ratio	0.89
2-Way Interaction	0.000
Temperature*Pressure (***TP***)	0.003
Temperature*Steam/GaN ratio	0.21
Pressure*Steam/GaN ratio	0.22

As can be seen in Table 2, the P-value for the temperature, pressure and their interaction is less than 0.05 showing that there is a meaningful correlation between these parameters and the ψ value. Also, the P-value for the general model is 0.001, which is again smaller than 0.05, showing that the developed ANOVA model is valid. Using regression analysis on the data obtained from the RSM model, the following equation was developed, which can predict the molar ratio of hydrogen to ammonia with R-square 0.97 with > 95% confidence interval:

$$(H_2{:}NH_3)\ ratio\ (\psi) = -24.4 + 0.001 \times PP \times 0.348 \times T - 3.04 \times P + 0.5 \times \varphi - 0.014 \times TP \quad (5)$$

The developed equation correlates the ψ value to the most sensitive operating parameters. This can help one to predict the final composition of the product produced by reactor R_2 without a need to apply a thermochemical equilibrium and RSM models, which are time-consuming to be established and used.

Figure 13 represents the effect of the binary interaction between the temperature and the pressure of the reactor R_2 on ψ value. As can be seen, three main regions are identified. In region I, in which 5 bar < P < 30 bar and T > 100 °C, the equilibrium model shows that the dominant product of the reactor is ammonia together with small contents of hydrogen, which can be separated through a low-temperature condenser. In region II, which has lower operating pressure (e.g. 5 to 10 bar), but higher temperatures (e.g. 200 °C to 300 °C), the co-production of hydrogen and ammonia is thermodynamically feasible while in region III, for a non-pressurised reactor, at T > 300 °C, hydrogen is the main product.

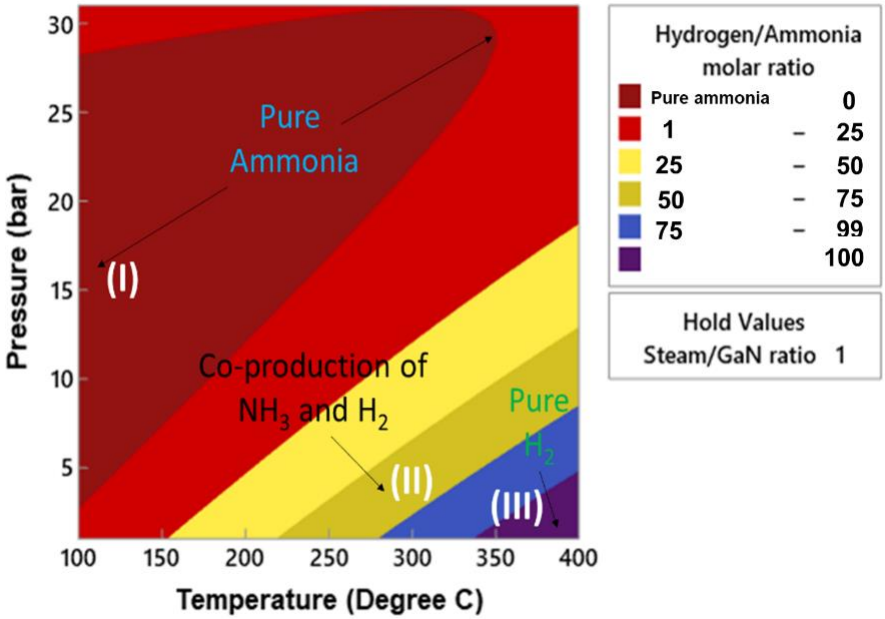


Fig. 13. Dependence of the final product of the process on operating temperature and pressure of reactor R_2.

Therefore, it is not recommended to pressurise reactor R_2 if the target product of the process is hydrogen. Figure 14 shows the calculated dependence of the sensitivity of ψ on the operating parameters of the reactor R_2. As can be seen, the target parameter is super-sensitive to the temperature-pressure interaction (*TP*) such that at a pressure of 1 bar, the sensitivity factor at *T*=200 °C is ~50, while it is suppressed to ~0.01 at *P*=16 and *P*=31 bar. Also, by increasing the temperature of the reactor, the sensitivity of ψ to *PT* interaction increases, however, at *P*=31 bar, the increase in the temperature of the reactor has no effect on the sensitivity factor. This means that at *P* >30 bar, the temperature of the reactor is not a key operating parameter and the performance of the reaction can be independent from the identified operating temperature range. For other interactions identified between the operating parameters such as the interaction between temperature and the φ value, the sensitivity factor is negative, showing that the reactor is not sensitive to the interaction between temperature and φ value. Also, for interaction between *P* and φ, for a range of pressure (17 to 31 bar), the sensitivity is zero or negative as well showing that pressuring the reactor has no effect on the target parameter. In light of the above discussion, using the equilibrium analysis and the RSM model, the optimised operating condition of the proposed process was estimated and represented in Table 3:

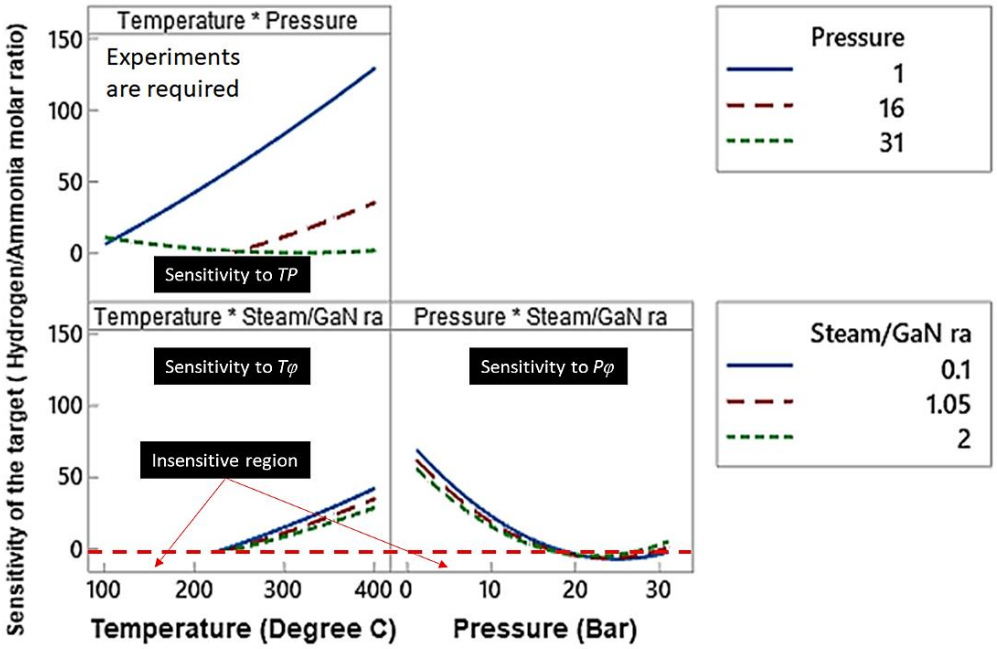


Fig. 14. Interaction analysis plot for the operating conditions of reactor R_2. In red regions, sensitivity was not identified as number of points were limited. Hence, experiments are required to identify the sensitivity trend.

Table 3. The optimised operating conditions obtained for the reactors.

Parameter		Value	unit
Reactor R_1*			
Temperature	100	°C	
Pressure	1	Bar	
Nitrogen/Ga ratio	0.5	[ ]	
Reactor R_2**			
Target parameter (ammonia is maximised):			
Temperature		100	°C
Pressure		5	Bar
Steam/GaN		1	[ ]
Target parameter (hydrogen is maximised)			
Temperature		400	°C
Pressure		1	Bar
Steam/GaN ratio		0.95	[ ]
Reactor R_3***			
Temperature		4730	°C
Pressure		1	Bar

*Kiln reactor, **Fluidised bed reactor, ***Plasma reactor.

3.5.Scalability study

Figure 15 presents the calculated dependence on production scale of the "exergy efficiency" shown with red colour and "thermal efficiency" shown with blue colour. As can be seen, by increasing the production scale of the process, the exergy efficiency of the system decreases. For example, for a small scale production of 5000 tonnes/year of ammonia, the exergy efficiency and thermal efficiency calculated for the system were 0.46 and 0.4, which decreased to 0.328 and 0.33 for a mid-scale (500000 tonnes/year). For a large scale production (1000000 tonnes/year), the value was 0.31 for both thermal and exergy efficiency. Hence, it can be stated that the proposed system is more suitable for decentralised fertiliser production, in which a small-scale plant is developed on-site according to the requirements, local community and specifications of the location to meet the sustainability criteria. Notably, the maximum theoretical thermal efficiency of the system is 0.8, which was calculated with Carnot efficiency equation [48].

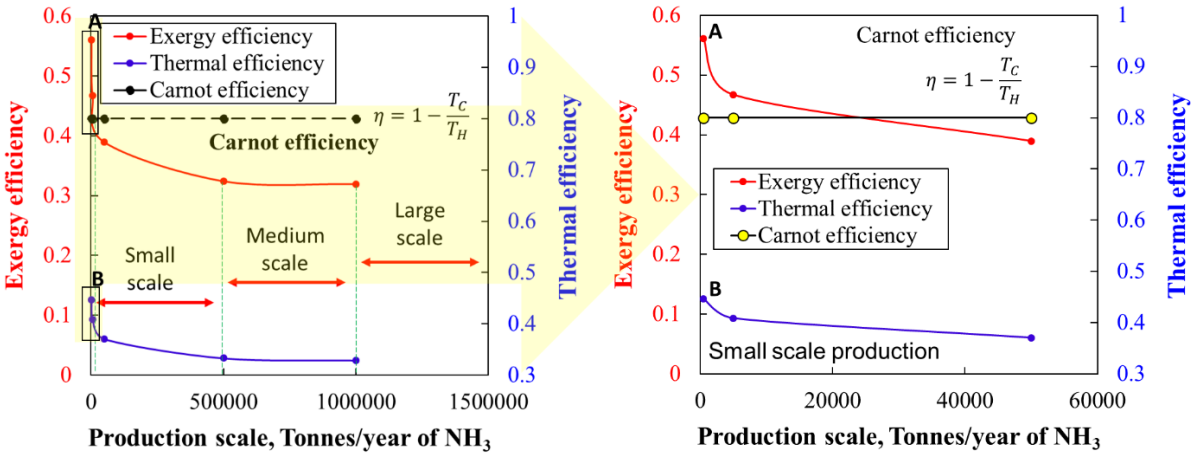


Fig. 15. Variation of exergy efficiency and thermal efficiency with production scale.

3.6.Thermal energy transferred to plasma reactor

Figure 16 represents the calculated thermal energy supplied with reactors R_1 and R_2 through primary heat transfer of GaN particles from reactor R_1 to reactor R_2 and secondary heat transfer from reactor R_2 to the plasma reactor via sensible heat absorbed by Ga_2O_3 particles. As can be seen in Figure 16, to minimise the exergy destruction between reactors R_1 and R_2, the operating temperatures of the reactors was considered the same to apply isothermal condition between the reactors, which in turn reduces the exergy destruction value to zero due to omitting the temperature difference between reactors. By considering the isothermal condition between reactors R_1 and R_2, the sensible heat can be transported from reactor R_1 to reactor R_2 and then is transported to the plasma reactor R_3.

An energy balance over the system showed that the maximum thermal energy of 12.3% can be supplied from other reactors, which is utilised for increasing the temperature of Ga_2O_3 particles. This also reduced the thermal load of the plasma reactor resulting in a decrease in its power consumption. It is possible to increase the temperature aiming at supplying more thermal energy to the plasma reactor, which is at cost of reducing the rate of ammonia production and increasing the rate of hydrogen production.

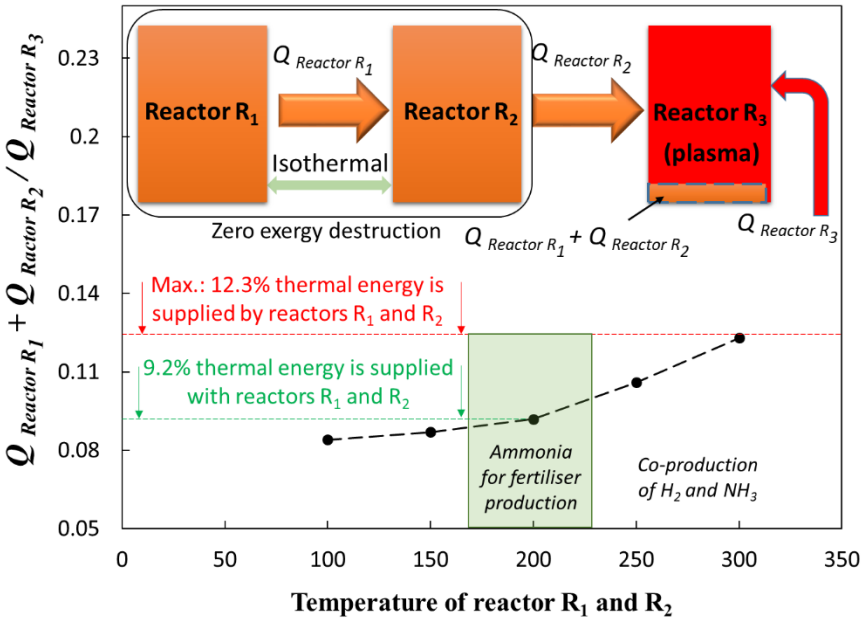


Fig. 16. The calculated thermal energy released from reactors R_1 and R_2 for supplying the plasma reactor.

4. Advantages, potential challenges and future works

The proposed process offers the following advantages in comparison with the current pathways for hydrogen and ammonia production:

1) ***Zero carbon process:*** The proposed process takes advantage of nitrogen fixation and does not involve any carbon-containing components, hydrogasification, partial oxidation of carbonaceous feedstock, water-gas shift, Boudouard and methanation reaction, which in turn offers a CO_2-neutral process for the production of clean fuels.
2) ***Sustainability:*** Thanks to the plasma reactor, the developed process offers a sustainable chain (loop) of chemical reactions from gallium to gallium nitride (via kiln reactor), gallium nitride to gallium oxide (via fluidised bed reactor) and gallium oxide to gallium (via plasma reactor). Reactors R_1 and R_2 are commercially available and the knowledge of handling gallium at T~400 °C has already been developed. The

products of the process are oxygen and hydrogen which are environmentally benign. For ammonia, the knowledge of handling and storage has already been developed. Considering the fact that the thermo-equilibrium chemical conversion of the reactors can reach the completion point, it can be stated that the theoretical limit for the chemical conversion extent of the reactors is the highest.

3) ***Flexibility in type of the clean fuel product:*** The system offers great flexibility in terms of the final products such that depending on the end-user requirements, the final product can be hydrogen, ammonia or a combination of both, which easily can be separated using a low-temperature condenser. Oxygen is also available as a side product, which can be dispatched to the market.

To harness the proposed process, the following challenges require further investigation:

1) ***Robust kiln reactor to handle liquid metals:*** Containing gallium in a kiln reactor at low-temperature operation is feasible through installing liners and cathode protection of the surface. However, such implementations can, in turn, induce a thermal resistance between the walls of the kiln reactor and the liquid metal. This decreases the thermal efficiency of the reactor. Therefore, a thorough assessment is highly recommended to evaluate the performance of the kiln reactor equipped with liner.

2) Robust nitrogen gas and steam injection technology for the reactors: A high-fidelity gas injection system is required for the kiln reactor to avoid agglomeration of GaN particles, while uniformly distributes the nitrogen gas in the reactor. Also, a robust steam injection system is required for the fluidised bed to maintain the fluidisation, heat and mass transfer rate.

3) ***Kinetic of the reactions in the plasma reactor:*** The proposed system requires a novel type of plasma reactor, which to the best of author's knowledge has not been developed yet. Hence, there is a lack of information on the design, configuration and performance of the reactor together with the lack of study on the kinetics of the gallium oxide dissociation in the plasma reactor.

4) ***Identification of new liquid metals:*** Although the proposed process is thermodynamically feasible using gallium as a potential option, it is highly recommended to identify other liquid metals which can potentially work in the system, thereby requiring further work to identify other plausible options.

5. Conclusions

In the present work, we reported the results of thermochemical equilibrium analysis to assess the feasibility and the thermodynamic potential of a novel process for co-production of hydrogen and ammonia using liquid metal and a plasma reactor. The process takes advantage of nitrogen fixation reaction, while offering a sustainable process, which eliminates the production of greenhouse gases. Thermochemical equilibrium and response surface methodology analysis showed that the process is thermodynamically feasible. Some of the advantages and main challenges were identified and the following conclusions were drawn:

- Within the identified operating conditions, the Gibbs free energy of the reactions in all reactors was negative showing that the reactions are spontaneous and feasible in the reactors. In reactors R_1 and R_2, the enthalpy of the reaction was negative, hence, the thermal energy released in the reactor can maintain the temperature and also be partially used to preheat the products before introducing to the plasma reactor. This can plausibly reduce the energy requirement of the plasma reactor.
- Thermodynamic assessment showed that the reactor R_2 can be used for the co-production of hydrogen and ammonia providing that the temperature, and feed ratio of the reactor (φ) is regulated such that 100 °C < T <400 °C, P=1 bar and 0.1 < φ < 1.0.
- The plasma reactor was found to be a plausible configuration to drive the dissociation reaction of Ga_2O_3, for which ΔG is highly positive. This reactor completes the circle of the reactions without emitting any greenhouse gases and environmental pollutants, which bring sustainability features to the process.
- Increasing the steam content in reactor R_2 can harm the quality of the product by producing Ga(OOH) instead of Ga_2O_3, which in turn decreases the mole fraction of gallium in the outlet of the plasma reactor.
- The response surface analysis showed that apart from temperature, pressure and feed ratio of the reactor, the interaction between temperature and pressure can also affect the performance of reactor R_2. Hence, a multi-response optimisation was conducted via a RSM model and the optimum operating conditions for the reactor, was identified.

Overall, the proposed process shows a great thermodynamic potential to be used for the nitrogen fixation and production of hydrogen and ammonia using plasma reactor. Despite plausible thermodynamic outcome, a series of experiments in accordance with the objectives defined in the “SCOPE” project, followed by an in-depth techno-economic assessment based

on the sustainability and business model developed in the "SCOPE" project is highly required to be conducted aiming at demonstrating the process and its feasibility. Also, an energetic assessment of the system based on the experimental data is highly recommended, which is ongoing and is a future target.

6. Outlook: How plasma-enabled disruptive process design could open industrial transformation

The SCOPE project, mentioned above, aims at industrial transformation of nitrogen fixation through innovative disruptive process design enabled by a plasma reactor, and to open tailored economic business windows of chemical plant conception, all under the umbrella of sustainability. While the plasma process considered here is entirely different from the plasma process of SCOPE, the above mentioned features – disruptive entire process design and new business windows – have a share and indeed were motivated by past studies leading to the conception of the SCOPE concept, and first unpublished studies undertaken in the frame of the project. We like to pinpoint possible industrial transformation scenarios, for which we were awarded, and will investigate and report them for the specific process design reported here in a follow-up study.

6.1 Green energy factors

Plasma processes principally can be run at small scale, as our previous studies[3] showed [35, 37]. From the embryonic insight revealed by the scalability study given in this paper it can be hypothesised that this might also apply to the process design enabled by the hot plasma reactor considered in this study. Small-scale (to be utilised on-site) nitrogen fixation production units offer the chance to adapt to the geographical locations; e.g. concerning the use of local green energy or to release agricultural benefits stemming from local factors [37].

6.2 Agro-environmental factors

Depending on the agricultural requirements of each geographical location such as soil conditions (pH value, nutrients, and soil grain size), rainfall, agricultural products and the size of the farms, the proposed process may be adjusted such that the power of the plasma reactor, type of the product, and quantity of ammonium-based products can be regulated. For example, if pH of soil is low, the nitrate of soil needs to be monitored and managed by using

[3] https://elements.evonik.com/wp-content/uploads/2019/05/Evonik_Elements_Edition_06_2016_Inspired_by_nature_EN.pdf

dilute fertiliser aiming at matching the nitrogen content of soil. Hence, the ammonia production via the process can be suppressed, while hydrogen production can be intensified to produce energy for soil mixers, water desalination units and their steam boilers together with supplying fuel for any energy-driven activities (e.g. water pumps, generators).

6.3 Social factors

The proposed process offers a green route for the production of fertiliser, ammonia and hydrogen, which is very well in-line with environmental policy of most of local governments. This may result in financial support of governments, such as financial support for use of sustainable processes in US [49] or China [50] or UK [51] . Also, the carbon zero (carbon neutral) footprint may promote the health and safety in the local community, which may suppress the cost associated with the pollution of water, soil, air and living species in the local nature. On top of that, operating small-scale plants at site of consumption rather than importing large-scale quantities of fertilisers, produced at another country, adds jobs on a local and national scale, which adds a governmental benefit to rural development. This is especially relevant in remote farming areas, such as given throughout Australia.

Acknowledgments

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